Available online at www.sciencedirect.com

ScienceDirect

Procedia Chemistry 17 (2015) 99 – 105

Procedia Chemistry

3rd International Seminar on Chemistry 2014

Bond Dissociation Energy of Halogen Oxides

Juliandri

Department of Chemistry, Universitas Padjadjaran, Jl. Raya Bandung-Sumdeang Km 21, Jatinangor 45363 Sumedang, Indonesia

Abstract

Bond Dissociation Energy (BDE) of halogen oxides have been studied theoretically. Density Functional Theory (DFT) functionals have been performed on the 6-311+G (2df) level of basis set. For comparison, the results of composite method G3B3 and available experimental data are used. In general both pure DFT functionals and hybrid methods predict excellent results for these energies. However, the hybrid method predictions are closer to experimental data than those of pure DFT functionals.

Keywords: BDE; DFT; Halogen Oxides

1. Introduction

Chemistry is based on the concept of chemical bonds. The breaking and making of chemical bonds are involved in most chemical reactions. Thus accurate data of bond dissociation energies (BDEs) is needed in bond strength prediction. A complete database of the experimental data of bond dissociation energies are also needed for comparison with the theoretical prediction.

The Density Functional Theory (DFT) hybrid methods perform better than the pure and local density approximation methods in the prediction of molecular geometries and energetics of halogen oxides XO, OXO and XO_2 species[1]. High spin contamination is a problem in certain open shell halogen oxides. Here, we use four DFT functionals (B3LYP, B3PW91, PBEPBE, and BLYP) to study the BDE of halogen oxides. Comparison is made with the composite method G3B3[2] instead of G3[3] due to poor performance of MP2 on fluorine oxide calculations[4]. The G3B3 composite method uses B3LYP optimum geometries for the single point high *ab initio* calculation series, while G3 uses MP2 geometries.

*Corresponding author. Tel.: +62-22-7794391.; fax: +62-22-7794391
E-mail Address: juliandri@unpad.ac.id

Peer-review under responsibility of Department of Chemistry, Faculty of Mathematics and Natural Sciences, Padjadjaran University
doi:10.1016/j.proche.2015.12.114

2. Computational Details

In 1983 the DFT was only a footnote in quantum chemistry textbooks[4,5]. The electronic structure methods that use the electronic density originally were developed by Thomas-Fermi (Bloch, 1929)[6] and Thomas-Fermi-Dirac (Dirac, 1930)[7]. Related work was also carried out by Gaspar (1954)[8] and Slater (1951)[9]. Modern DFT is based on a remarkable result by Hohenberg and Kohn (1965)[10] in which without loss of rigor the ground state expectation values of all quantum mechanical observables are written as functionals of the electronic ground-state density ρ(r). Through the application of the variational principle Hohenberg and Kohn proved that, up to a trivial constant, there exists a one-to-one mapping between the external potential and the ground-state electron density. In order to present a summary of DFT we suggest the reader to follow the approach of Scuseria (2005)[11].

The DFT is well known for its accuracy and economy in regard to computational effort[12]. Comparison is made with high levels of ab initio calculation, G3 calculations[13], G3B3 calculations[2] and experimental data where available. The equilibrium geometry of non-closed shell compounds is accepted as realistic if spin contamination is less than 10 percent. All calculations were performed using Gaussian 03 packages[14] and all DFT calculations were carried out using the 6-311+G(2df)[15,16] level of basis set. Four different DFT functionals have been used to study the geometries and energetics of the Bromine oxides. The pure DFT functional BLYP[17] and PBEPBE[18], and hybrid methods B3LYP[19] and B3PW91[20] were selected to perform the studies.

3. Results and Discussion

The bond dissociation energy of fluorine oxides is determined as the energy difference for the reaction $FO_n (n = 1-3) \rightarrow FO_{n-1} + O$. The neutral FO_n bond dissociation energies are shown in Table 1. The experimental values of the bond dissociation energy are derived from the experimental heats of formation[21]. The B3LYP and B3PW91 bond dissociation energy predictions are in very good agreement with the experimental and G3B3 values. For the FO bond dissociation energy, both functionals predict results only 0.09 eV different from the experimental value. The PBEPBE prediction is 1 eV larger than that of the experimental value. For FOO, similar accuracy is also shown by B3LYP and B3PW91. The bond dissociation energy predicted by B3PW91 is only 0.04 eV larger than that of experiment, while the B3LYP predicts a value similar to the experimental value.

Table 1. Bond Dissociation Energies for FO_n Species (in eV)

Reactions	**Methods**					
	B3LYP	B3PW91	PBEPBE	BLYP	G3B3	Exp*
$FO \rightarrow F + O$	2.33	2.33	3.27	2.87	2.29	2.24
$FOO \rightarrow FO + O$	3.40	3.44	4.37	4.10	3.42	3.40
$FOOO \rightarrow FOO + O$			2.14	1.95		

*Derived from the experimental heats of formation[21].

The bond dissociation energies of FO_n^+ and FO_n^- are shown in Tables 2 and 3, respectively. The experimental values of the dissociation energy are derived from the experimental heats of formation of molecules that taken from reference[21]. The BLYP and PBEPBE predictions of bond dissociation energies are higher than that of experiment as shown in the tables. As found for the neutral species, B3LYP and B3PW91 perform better than BLYP and PBEPBE. In the case of FO_n^+ the DFT functional predictions are higher than the experimental values, except for the $FOO^+ \rightarrow FO^+ + O$ by B3LYP and B3PW91. From Table 2 we can conclude that dissociation of cation fluorine oxides to O^+ is more favorable than to O.

Table 2. Bond Dissociation Energies for Cation FO_n^+ Species (in eV)

Reactions	Methods					
	B3LYP	B3PW91	PBEPBE	BLYP	G3B3	Exp*
$FO^+ \rightarrow F + O^+$	3.57	3.54	4.77	4.35	3.13	3.10
$FOO^+ \rightarrow FO + O^+$	4.73	4.67	6.14	5.88	4.70	4.43
$FOOO^+ \rightarrow FOO + O^+$	4.49	4.41	5.21	5.07	4.12	
$FO^+ \rightarrow F^+ + O$	7.17	7.18	8.15	7.91	6.97	6.91
$FOO^+ \rightarrow FO^+ + O$	3.49	3.46	4.64	4.40	3.86	3.57
$FOOO^+ \rightarrow FOO^+ + O$	3.17	3.18	3.44	3.29	2.85	

*Derived from the experimental heats of formation[21].

Table 3. Bond Dissociation Energies for Anion FO_n^- Species (in eV)

Reactions	Methods					
	B3LYP	B3PW91	PBEPBE	BLYP	G3B3	Exp*
$FO^- \rightarrow F + O^-$	3.01	3.00	3.78	3.57	3.20	3.05
$FOO^- \rightarrow FO + O^-$	5.03	4.13	3.41	5.48	4.96	
$FOOO^- \rightarrow FOO + O^-$	2.97	3.02	3.61	3.55	3.32	
$FO^- \rightarrow F^- + O$	1.16	1.11	1.63	1.53	1.13	1.11
$FOO^- \rightarrow FO^- + O$	4.35	3.46	5.02	4.78	4.05	
$FOOO^- \rightarrow FOO^- + O$	1.33	2.32	2.45	2.17	1.79	

*Derived from the experimental heats of formation[21].

For the FO_n^- bond dissociation energies, the DFT functional predictions are in very good agreement with experimental values. PBEPBE predicts the bond dissociation energy higher than other functionals. In the case of $FO^- \rightarrow F + O^-$, the functional prediction is 0.73 eV higher than experimental value. The bond dissociation energies predicted by the hybrid method calculations are close to the experimental values than those of pure DFT functionals. However the dissociation of anion fluorine oxides to O is more favoured than to O^-.

The neutral ClO_n bond dissociation energies are shown in Table 4. The bond dissociation energy is determined as the energy difference for the reaction, $ClO_n (n = 1-3) \rightarrow ClO_{n-1} + O$. The B3LYP and B3PW91 bond dissociation energy predictions are in very good agreement with the experimental results and the G3B3 values. The experimental values of the bond dissociation energy are derived from the experimental heats of formation[22]. For the ClO bond dissociation energy, B3LYP predict a result that only 0.01 eV different from the experimental value (2.75 eV). Both BLYP and PBEPBE predict higher energies. For the ClOO bond dissociation energies we only have BLYP and PBEPBE results due to spin contamination on ClOO calculation by hybrid methods. Our bond dissociation energies prediction is 0.7-0.9 eV higher than that of experimental value. For the ClO_3 bond dissociation energies all functionals prediction are in very good agreement with the experimental value.

Table 4. Bond Dissociation Energies for ClO_n Species (in eV)

Reactions	Methods						
	B3LYP	B3PW91	PBEPBE	BLYP	G3B3	Exp*	BP86**
$ClO \rightarrow Cl + O$	2.76	2.82	3.41	3.22	2.72	2.75	3.15
$ClOO \rightarrow ClO + O$			3.44	3.23		2.57	3.58
$OClO \rightarrow ClO + O$	2.26	2.42	3.18	2.77	2.54	2.58	2.62
$ClOOO \rightarrow ClOO + O$			2.98	2.72			2.81
$ClO_3 \rightarrow OClO + O$	1.26	1.42	1.98	1.57	1.55	1.51	1.49

*Derived from the experimental heats of formation[21,22,23]

The bond dissociation energies of ClO_n^+ and ClO_n^- are shown in Tables 5 and 6, respectively. The experimental values of the dissociation energy are derived from the experimental heats of formation various molecules taken from reference[21]. The BLYP and PBEPBE prediction of bond dissociation energies are higher than experiment as shown in the Tables. As found for the neutral species, B3LYP and B3PW91 perform better than BLYP and PBEPBE. In the case of ClO_n^+ the pure DFT functional predictions are always higher than the experimental values, except for the $OClO^+ \rightarrow ClO^+ + O$ by BLYP. Due to spin contamination we cannot calculate the bond dissociation energies involving ClOO using hybrid methods.

Table 5. Bond Dissociation Energies for ClO_n^+ Species (in eV)

Reactions	Methods					
	B3LYP	B3PW91	PBEPBE	BLYP	G3B3	Exp*
$ClO^+ \rightarrow Cl + O^+$	5.99	5.93	6.80	6.72	5.52	5.49
$ClOO^+ \rightarrow ClO + O^+$	5.15	5.00	5.97	5.95	4.99	
$OClO^+ \rightarrow ClO + O^+$	5.55	5.59	6.73	6.41	5.72	5.88
$ClOOO^+ \rightarrow ClOO + O^+$			6.97	6.85		
$ClO_3^+ \rightarrow OClO + O^+$	4.10	4.18	5.14	4.77		3.73
$ClO^+ \rightarrow Cl^+ + O$	4.90	4.99	5.70	5.45	6.33	4.84
$ClOO^+ \rightarrow ClO^+ + O$	1.92	1.89	2.58	2.45	3.30	
$OClO^+ \rightarrow ClO^+ + O$	2.32	2.48	3.34	2.91	4.03	3.14
$ClOOO^+ \rightarrow ClOO^+ + O$	3.60	3.68	4.45	4.12	3.84	
$ClO_3^+ \rightarrow OClO^+ + O$	0.81	1.01	1.59	1.13	0.98	0.44

*Derived from the experimental heats of formations[21].

For the bond dissociation energy of ClO^+ the hybrid method predictions are in very good agreement with the experimental values, but the predictions are lower than experimental values on the $OClO^+$ dissociation energy. In the case of $ClOOO^+$ we only compare the results with the G3B3 prediction. The hybrid method predictions are also better than those of pure DFT functional. For the symmetric ClO_3^+ bond dissociation energy our DFT predictions are higher than the experimental value, and the B3LYP predicts better than other functionals. The dissociation to neutral O is more favourable than that to cation O.

In the case of ClO_n^- the DFT functional predictions of bond dissociation energies are in good agreement with the experimental values. We cannot calculate the dissociation energies for reaction involving ClOO due to spin contamination at hybrid method calculations. The prediction of ClO^- bond dissociation energies by both hybrid and pure DFT functionals are in very good agreement each other and with the experimental data. However the hybrid methods perform better than pure DFT functionals.

Table 6. Bond Dissociation Energies for ClO_n^- Species (in eV)

Reactions	Methods						
	B3LYP	B3PW91	PBEPBE	BLYP	G3B3	Exp*	BP86**
$ClO^- \rightarrow Cl + O^-$	3.40	3.54	3.91	3.79	3.66	3.57	3.54
$ClOO^- \rightarrow ClO + O^-$	3.53	3.56	4.10	4.05	3.74		5.09
$OClO^- \rightarrow ClO + O^-$	2.88	3.06	3.50	3.23	3.39	3.50	2.96
$ClOOO^- \rightarrow ClOO + O^-$			3.73	3.30			2.80
$ClO_3^- \rightarrow OClO + O^-$	3.79	3.99	4.20	3.89	4.43	4.31	3.68
$ClO^- \rightarrow Cl^- + O$	1.32	1.34	1.87	1.68	1.39	1.41	1.58
$ClOO^- \rightarrow ClO^- + O$	2.88	2.85	3.60	3.48	2.80		4.70
$OClO^- \rightarrow ClO^- + O$	2.24	2.35	3.00	2.66	2.45	2.67	2.57
$ClOOO^- \rightarrow ClOO^- + O$	2.32	2.39	3.24	2.96	2.43		2.02
$ClO_3^- \rightarrow OClO^- + O$	3.17	3.34	3.88	3.43	3.58	3.37	3.35

*Derived from the experimental heats of formations[21,22]

In the case of $OClO^-$ the pure DFT functional predictions are better than those of hybrid methods. The hybrid methods overestimate the bond dissociation energies. For symmetric ClO_3^- the pure DFT also perform better than the hybrid methods. As with ClO_n^+ bond dissociation energies, dissociation to neutral O is more favourable than to anion O.

Table 7. Bond Dissociation Energies for BrO_n Species (in eV)

Reactions	Methods					
	B3LYP	B3PW91	PBEPBE	BLYP	Exp*	BP86**
$BrO \rightarrow Br + O$	2.54	2.56	3.25	3.04	2.40	3.05
$BrOO \rightarrow BrO + O$			3.53	3.29	2.74	3.56
$OBrO \rightarrow BrO + O$	2.07	2.17	3.00	2.67	2.27	2.81
$BrOOO \rightarrow BrOO + O$			2.90	2.66		2.82
$BrO_3 \rightarrow OBrO + O$	1.14	1.24	1.89	1.57	1.82	1.60

*Derived from the experimental heats of formations[21,22]

The neutral BrO_n bond dissociation energies are shown in Table 7. The bond dissociation energy is determined as the energy difference for the reaction $BrO_n (n = 1-3) \rightarrow BrO_{n-1} + O$. The B3LYP and B3PW91 bond dissociation energy predictions are in very good agreement with the experimental values, derived from the experimental heats of formation[21,22]. For the BrO bond dissociation energy, B3LYP predict a result that only 0.14 eV different from the experimental value (2.40 eV). Both BLYP and PBEPBE predict higher energies. For the BrOO bond dissociation energies we only have BLYP and PBEPBE results due to spin contamination on BrOO calculation by hybrid methods. For the symmetric BrO_3 bond dissociation energies, the PBEPBE prediction is the best. The pure DFT functional predictions are more accurate than those of hybrid method.

The bond dissociation energies of BrO_n^+ and BrO_n^- are shown in Tables 8 and 9, respectively. The experimental values of the dissociation energy are derived from the experimental heats of formation various molecules taken from reference[21]. For the BrO_n^+, the BLYP and PBEPBE prediction of bond dissociation energies are much higher than available experiment data as shown in the Tables. As found for the neutral species, B3LYP and B3PW91 perform better than BLYP and PBEPBE. In the case of BrO_n^+ the pure DFT functional predictions are always higher than the hybrid method predictions. However the pure DFT functional predictions for the $OBrO^+ \rightarrow BrO^+ + O$ are better than those of hybrid method. Due to spin contamination we can not calculate the bond dissociation energies involving BrOO on hybrid methods.

Table 8. Bond Dissociation Energies for BrO_n^+ Species (in eV)

Reactions	Methods				
	B3LYP	B3PW91	PBEPBE	BLYP	Exp*
$BrO^+ \rightarrow Br + O^+$	6.22	6.11	7.12	7.04	5.57
$BrOO^+ \rightarrow BrO + O^+$	5.79	5.72	6.91	6.79	
$OBrO^+ \rightarrow BrO + O^+$	5.43	5.39	6.68	6.47	5.61
$BrOOO^+ \rightarrow BrOO + O^+$			7.19	7.10	
$BrO_3^+ \rightarrow OBrO + O^+$	3.59	3.58	4.70	4.46	
$BrO^+ \rightarrow Br^+ + O$	4.01	4.03	4.87	4.66	3.76
$BrOO^+ \rightarrow BrO^+ + O$	2.11	2.18	3.05	2.80	
$OBrO^+ \rightarrow BrO^+ + O$	1.75	1.85	2.82	2.47	2.44
$BrOOO^+ \rightarrow BrOO^+ + O$	3.25	3.24	3.81	3.60	
$BrO_3^+ \rightarrow OBrO^+ + O$	0.22	0.36	1.03	0.66	

*Derived from the experimental heats of formations[21,22]

In the case of BrO_n^- the DFT functional predictions of bond dissociation energies are in good agreement with the experimental values. We can not calculate the dissociation energies for reaction involving BrOO due to spin contamination on hybrid method calculations. The prediction of BrO^- bond dissociation energies by both hybrid and pure DFT functionals are in very good agreement each other and with the experimental data. However the hybrid methods perform better than pure DFT functionals.

In the case of bond dissociation energies of BrO_n^+ and BrO_n^-, the separation to neutral O is more favourable than ionic O as shown in Table 8 and 9. Similar features are also found on the ionic chlorine and fluorine oxides bond dissociation energies as discussed in previous section.

Table 9. Bond Dissociation Energies for BrO_n^- Species (in eV)

Reactions	Methods					
	B3LYP	B3PW91	PBEPBE	BLYP	Exp*	BP86**
$BrO^- \rightarrow Br + O^-$	3.28	3.40	3.84	3.68	3.29	3.55
$BrOO^- \rightarrow BrO + O^-$	4.74	4.87	5.09	4.97		5.03
$OBrO^- \rightarrow BrO + O^-$	2.95	3.12	3.56	3.33	3.30	3.29
$BrOOO^- \rightarrow BrOO + O^-$			3.68	3.63		3.84
$BrO_3^- \rightarrow OBrO + O^-$	4.03	4.21	4.44	4.17		4.16
$BrO^- \rightarrow Br^- + O$	1.33	1.33	1.88	1.71	1.39	1.75
$BrOO^- \rightarrow BrO^- + O$	4.00	4.04	4.50	4.34		4.53
$OBrO^- \rightarrow BrO^- + O$	2.22	2.28	2.98	2.70	2.41	2.79
$BrOOO^- \rightarrow BrOO^- + O$	1.46	1.44	2.13	1.95		4.11
$BrO_3^- \rightarrow OBrO^- + O$	3.14	3.26	3.88	3.50		3.68

*Derived from the experimental heats of formations[21,22,24]

Conclusions

Theoretical predictions of bond dissociation energies of FO_n, FO_n^+, and FO_n^- are also studied. Both pure DFT functionals and hybrid methods predict excellent results for these energies. However the hybrid method predictions are closer to experimental data than those of pure DFT functionals. Bond dissociation energies of ClO_n, ClO_n^+, and ClO_n^- are studied. The DFT functional predictions are in very good agreement with the experimental data. Especially PBEPBE functional sometimes predicts higher value than other functionals and experimental data. Bond dissociation energies of BrO_n, BrO_n^+, and BrO_n^- are studied. The DFT functional predictions are in very good

agreement with the experimental data. The PBEPBE functional sometimes predicts higher values than other functionals and experimental data.

Acknowledgements

Authors are gratefully acknowledge the facility supports from the Department of Chemistry, Padjadjaran University, Bandung, Indonesia.

References

1. Juliandri, Density Functional Calculations on XO_3, XO_3^+, XO_3^- (X= F, Cl, Br), PhD Thesis, Newcaste University, Newcastle upon Tyne, 2008.
2. Baboul A. G., L. A. Curtiss, P. C. Redfern, and K. Raghavachari, Gaussian-3 theory using density functional geometries and zero-point energies, *J. Chem. Phys.,* 1999, 110, 7650.
3. Curtiss L. A., K. Raghavachari, P. C. Redfern, V. Rassolov, J. A Pople, Gaussian-3 (G3) theory for molecules containing first and second-row atoms, *J Chem Phys*, 1998, 109, 7764.
4. Ventura O. N. and M. Kieninger, The FO_2 radical: a new success of density functional theory, *Chem. Phys Lett*., 1995, 245, 488.
5. Parr R. G., Density Functional Theory, *Annu. Rev. Phys. Chem*., 1983, 34, 631.
6. Bloch F., Bemerkung zur Elektronentheorie des Ferromagnetismus und der elektrischen Leitfähigkeit, *Z. Phys*., 1929, 57, 545.
7. Dirac P. A. M., Note on Exchange Phenomena in the Thomas Atom, *Proc. Camb. Phil. Soc*., 1930, 26, 376.
8. Gaspar R., Über eine approximation des Hartree-Fockschen potentials durch eine universelle potentialfunktion, *Acta Phys. Hung*., 1954, 3, 263.
9. Slater J. C., A simplification of the Hartree-Fock method, *Phys. Rev*., 1951, 81, 385.
10. Hohenberg P. and W. Kohn, Inhomogeneous Electron Gas, *Phys. Rev*. B, 1964, 136, 864 and W. Kohn and L. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, *Phys. Rev*. A, 1965, 140, 1133.
11. Scuseria G. E. and V. N. Staroverov, in *Theory and Applications of Computational Chemistry*; The First Forty Years, C. Dykstra et al ed, Elsevier, Amsterdam, 2005.
12. Koch W. and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, 2nd ed, Wiley, Weinheim, 2000.
13. Curtiss L. A., M. P. McGrath, J. P. Blaudeau, N. E. Davis, R. C. Binning, Jr., and L. Radom, Extension of Gaussian-2 theory to molecules containing third-row atoms Ga–Kr, *J. Chem. Phys*. 1995, 103, 6104.
14. Frisch M. J., et al , Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.
15. Krishnan R., J. S. Binkley, R. Seeger, and J. A. Pople, Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions, *J. Chem. Phys*. 1980, 72, 650.
16. McLean A. D. and G. S. Chandler, Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, *Z*=11–18, *J. Chem. Phys*. 1980, 72, 5639.
17. Becke A. D., Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev*. A, 1988, 38, 3098.
18. Perdew J. P., K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett*., 1996, 77, 3865.
19. Stephens P. J., F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields, *J. Phys. Chem*., 1994, 98,11 623.
20. Perdew J. P., K. Burke, and Y. Wang, Generalized gradient approximation for the exchange-correlation hole of a many-electron system, *Phys. Rev*. B, 1996, 54, 16533.
21. Chase M. W. Jr., NIST-JANAF Thermochemical Tables, *J. Phys. Chem. Ref. Data*, 1998 Mono 9 Suppl 1.
22. Atkinson R., D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, M. J. Rossi, and J. Troe, Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement VIII, Halogen Species Evaluation for Atmospheric Chemistry, *J. Phys. Chem. Ref. Data,* 2000, 29, 167.
23. Li Q., S. Lu, W. Xu, Y. Xie, and H.F. Schaefer, Molecular Structures and Electron Affinities for the Chlorine Oxides ClOO, ClOOO, and ClO_3 (C_{3v}), *J. Phys. Chem*. A, 2002, 106, 12324.
24. Xie Y., H.F. Schaefer, Y. Wang, X. Fu, and R. Liu, Electron affinities of the bromine oxides BrO_n, n = 1-4, *Mol. Phys*, 2000, 98, 879.